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# **Field Evaluation of Sediment Structure and Content Relative to Associated Hydrates**

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14. ABSTRACT  The objective of work reviewed through this report is to provide a natural system database to assist in developing a hydrate dissociation simulator. This work was conducted primarily on samples previously taken in the Cascadia Margin (CM) and Gulf of Mexico (GOM). Cascadia Margin is an accretionary prism of a subduction zone. The sample region in the Gulf of Mexico is a salt basin that formed from Late Triassic rifting of the Pangea super continent, and flooding by a thick salt deposit during Middle Jurassic marine incursions. To contribute to the development of the simulator, data from analysis of the samples provide information on the range of sediment structure and characteristics of the sediments.  In the GOM, cores were taken over two locations, Bush Hill and GC234, that have active hydrate beds at the sediment water-column interface. Sampling was with push cores during submarine dives. Four different sites were cored with a 10-m piston in the CM. One site was a vent region of blank seismic reflection believed to be vertical channels. Another site has a sharp scarp observed through previous surveys. Cores from this location contained hydrates. Coring was also performed where a fishing boat recently pulled up surface hydrates in the net. A final site was a control with no hydrates.				
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## Table of Contents

Table of Contents .....	iii
Research Objective.....	1
Introduction .....	1
Methods.....	3
Results and Discussion.....	4
Summary .....	11
Literature Cited.....	11

# FIELD EVALUATION OF SEDIMENT STRUCTURE AND CONTENT RELATIVE TO ASSOCIATED HYDRATES

## Research Objective:

The objective of work reviewed through this report is to provide a natural system database to assist in developing a hydrate dissociation simulator.

## 1. Introduction:

The goal of the first year in the program is to initiate sample analysis of hydrates and sediments to provide a database that will contribute to the development of a hydrate dissociation simulator. This work was conducted primarily on samples previously taken in the Cascadia Margin (CM) and Gulf of Mexico (GOM). In addition there is some comparison with data from samples taken in 1998 on the Haakon-Mosby Mud Volcano (HMMV) in the Norwegian-Greenland Sea. Comparison of these sites will provide a broad range of in-situ data for development of the simulator. The HMMV is a cold seep off the coast of Norway with an active mud flow. Cascadia Margin is an accretionary prism of a subduction zone. The structure of this region has resulted in a recent tectonic compression and deformation. Hydrates in this region are found in silty clays and clayey silts interbedded with fine sand turbidites. The sample region in the Gulf of Mexico is a salt basin that formed from Late Triassic rifting of the Pangea super continent, and flooding by a thick salt deposit during middle Jurassic marine incursions. Thermogenic petroleum and gas deposits were produced from Miocene to Pleistocene reservoirs in the region. In this region over pressured fracture zones that surround moving salt diapirs and sheets provide active conduits for vertical migration from deep reservoirs to shallow pools and the surface. In this system hydrates are present in organic rich silty clays. To contribute to the development of the simulator, data from analysis of the samples provide information on the range of sediment structure and characteristics of the sediments, between these distinctly different regions. This will assist in understanding the range in dissociation behaviors and modeling the process.

Sample analysis in this report employs stable carbon isotopes to trace carbon cycling that influences the methane hydrate formation, stability and fate. Stable carbon isotope ratios vary as a function of the source of  $\text{CO}_2$  that is transferred into organic matter through the autotrophic cycle, the enzymatic reaction in  $\text{CO}_2$  fixation (Estep et al. 1978) and the rate that  $\text{CO}_2$  is transferred into organic matter (Fogel et al. 1993). The  $\delta^{13}\text{C}$  of contributing  $\text{CO}_2$  sources have a broad range from approximately 0‰ to -50‰. A substantial source of oceanic  $\text{CO}_2$  is atmospheric. The  $\delta^{13}\text{C}$  of atmospheric  $\text{CO}_2$  is approximately -7‰ depending on the region of the world. If atmospheric  $\text{CO}_2$  is cycled by terrestrial plants there is an isotopic fractionation that occurs during the fixation that provides a range in  $\delta^{13}\text{C}$  of approximately -30‰ to -12‰. The more depleted  $^{13}\text{C}$  value occurs in organisms that fix  $\text{CO}_2$  via the Calvin-Benson cycle (Whelan et al., 1973), while relatively more  $^{13}\text{C}$  enrichment occurs with  $\text{CO}_2$  fixation through the Hatch-Slack pathway (Estep et al. 1978). In the ocean  $\text{CO}_2$  values are isotopically enriched to a range of -2‰ to 2‰ as a function of carbonate equilibrium. This results in enriched  $^{13}\text{C}$  isotope signatures in marine phytoplankton that range between -18‰ and -30‰ (Gearing et al., 1977;

Sackett, 1991; Rau et al., 1989; 1991). In ocean sediment pore waters, active reduction of CO<sub>2</sub> results in a depleted <sup>13</sup>C isotope signature. In regions of ocean sediment with active biological methane cycling, the δ<sup>13</sup>C of the CO<sub>2</sub> can be as isotopically depleted as -50‰. This wide range in the δ<sup>13</sup>C for CO<sub>2</sub> results in distinct isotope signatures between thermogenic and biogenic methane. Biogenic methane has been reported to be light in δ<sup>13</sup>C with a range of -85‰ to -103‰ (Borowski et al., 1996; Borowski et al., 1997), with the lower value indicative of more active biogenic methane production. Thermogenic methane is substantially more enriched in <sup>13</sup>C with values in the range of -36‰ to -40‰ (Sassen and MacDonald, 1997).

### 3. Approach:

In the GOM cores were taken over two locations that have active hydrate beds at the sediment water column interface. The Bush Hill and GC234 site coordinates are listed in Table 1. Sampling in the GOM was with push cores during submarine dives and surface sediment grabs. Typically 0.5-m cores were taken in the GOM and surface samples were obtained from these cores. Four different sites were sampled in the CM with a wide range in the hydrate abundance (Table 1). Cores were taken with a 10-m piston corer and ranged from 2 to 8-m. For the CM cores 10-20 sub-samples were obtained through the core profile. Cores C1 and C6 were taken at vent site with a region of blank seismic reflection which is believed to be vertical channels. Core C7 was taken at a site that was found to have a sharp scarp through previous seismic surveys. Cores from this location contained hydrates. Coring at C9 was in a region that a fishing boat recently pulled up a large load of surface hydrates in the net. Hydrates were not found in cores at region C9.

Table 1: Core sampling locations on the Texas-Louisiana Shelf in the Gulf of Mexico and Cascadia Margin along the coast of British Columbia, Canada.

Station	Position	Water Depth (m)
Cascadia Margin C1	48°40.044'N, 126°50.751'W	1267
Cascadia Margin C6	48°39.966'N, 126°55.178'W	1265
Cascadia Margin C7	48°40.047'N, 126°51.067'W	1264
Cascadia Margin C9	48°40.099'N, 126°50.751'W	840
Gulf of Mexico Bush Hill (BH)	27° 46.956'N, 91° 30.483'W	550
Gulf of Mexico GC234	27° 44.767'N, 91° 13.321'W	570

#### 4. Methods:

Work combines basic physical and chemical parameters analysis to investigate the sediment structure and content. The following methods were applied to the sample analyses.

##### a.) Stable Carbon Isotope ( $\delta^{13}\text{C}$ ) Analysis

Stable carbon isotope analysis was conducted with samples in gas and solid phases. The  $\delta^{13}\text{C}$  was measured with a Finnigan Delta S isotope ratio mass spectrometer (IRMS). Sediment samples were introduced to the IRMS with combustion in a Carlos Erba CNS 1000 instrument. Stable carbon isotope analysis for methane to hexane gases and carbonate is conducted with a gas phase inlet isotope ratio mass spectrometer. The gas chromatograph used was the Varian Star 3400 CX which is constructed to run samples (Varian, Harbor City, CA) in a parallel line with a Finnigan Magnum ion trap and a Finnigan Delta-S isotope ratio mass spectrometer (GC/ITMS/IRMS, Finnigan Corporation, San Jose, CA). The effluent from the column was split, 10% going to the ITMS for peak identification and the remainder to the IRMS where the analytes were combusted in line at 940 °C to  $\text{CO}_2$  for isotope analysis. The two mass spectrometers provide peak identification simultaneous with the isotope analysis. The temperature profile through the GC runs started at 40°C and ramped to 180°C over 8 minutes. The  $\delta^{13}\text{C}$  standard was Pee Dee Belemnite. For the isotope ratio mass spectrometer, the detection limit is 1 µg C and the precision is  $\pm 0.3$  ‰.

##### b.) Sediment Structure Analysis

Data presented here include sediment organic carbon content and grain size. Sediment grain size is broken into 3 phases with sand 2000 – 62 µm, silt 64 to 4 µm, and clay less than 4 µm (Ingram, 1971; Galehouse, 1971). At each core depth, 15-20 gm of sediment was sub-sampled from cores and treated with 30%  $\text{H}_2\text{O}_2$  for 48-hr and subsequently washed with milli-Q water. Samples were then dispersed with 50 gm/l Calgon solution and wet sieved at 4 phi to separate sand and mud fractions. The mud fraction was then suspended in 1 L of DI water and samples were with drawn based on settling times according to the Stoke's Law. Sand fraction was generally less than 5% of bulk weight for all samples. The settling time provided data at 4, 4.5, 5.5, 6, 7, 8, and 9 phi which corresponds to 64, 44, 31, 22, 16, 7.8, 3.9 and 1.95 µm, respectively. Vibration in the laboratory inhibited analysis of smaller particles.

Analysis of organic carbon content required volatilization of the inorganic carbon. This was accomplished by placing dried sediments in a bell jar with concentrated hydrochloric acid vapor on the jar base for 24 hours. After removal of the inorganic carbon, samples were dried a second time. Weighed sub-samples, approximately 5 mg, were run through the Carlos Erba sample introduction system for carbon isotope analysis and carbon content. All samples were run in triplicate.

c.) Organic Sediment  $\delta^{13}\text{C}$

Sediments were treated as described for carbon content in section 4b and analyzed on the mass spec described in 4a. All samples were run in triplicate.

d.) Hydrate Content

The hydrate samples were placed in a 30 ml serum bottle and argon gas was streamed into the bottle to remove  $\text{CO}_2$  in the air. Samples were sealed with aluminum and rubber septa. After the hydrates dissociated, 10-20  $\mu\text{l}$  samples were taken with a 100  $\mu\text{l}$  gas tight syringe from the bottles and injected into a GC. Samples were analyzed for methane, ethane, propane, butane, pentane and hexane concentrations. All samples were run in triplicate.

e.) Hydrate  $\delta^{13}\text{C}$

For  $\delta^{13}\text{C}$  of gases in the hydrates samples were prepared as described in section 4d. Gases were injected into the mass spectrometer described in section 4a. Gases that were analyzed included methane, ethane, propane, butane, pentane, hexane and carbon dioxide. All samples were run in triplicate.

f.) Bicarbonate  $\delta^{13}\text{C}$

Dried sediment were place in serum bottles and capped using the procedure described in section 4b. The samples were treated with 800  $\mu\text{l}$  85% phosphoric acid. The  $\text{CO}_2$  in the serum bottle was removed with a gas tight syringe and injected in GC (section 4a) with the method described for methane analysis (section 4e). All samples were run in triplicate.

## 5. Results and Discussion

a). Sediment Properties

The data for sediment properties includes the organic carbon content analyzed on samples from the Cascadia Margin and Gulf of Mexico and grain size analysis on samples from the Cascadia Margin. The percent organic carbon in the Cascadia Margin cores from stations C1, C6 and C9 ranged between 0.390 and 0.738% (Table 2). There was not a large variation between these sites or through the individual cores. These values were lower than expected for the presence of hydrates. Future work will need to address the vertical methane migration relative to the microbial formation at the sample depth. The GOM samples are from two sites with large amounts of hydrates at the sediment-water column interface. At these sites the %C ranges from 1.25 to 17.07%. The high values are associated with regions of petroleum seeps through the ocean floor.



Table 2: Analysis of percent organic carbon in sediments from the Gulf of Mexico and Cascadia Margin.

Core Site	Depth (cm)	% C	% C	% C	Average	s.d.
Cascadia Margin						
C9	5-10	0.500	0.500	0.483	0.494	0.010
C9	15-20	0.611	0.592	0.583	0.595	0.014
C9	25-30	0.537	0.525	0.547	0.536	0.011
C9	35-40	0.481	0.470	0.456	0.469	0.013
C9	45-50	0.359	0.343	0.360	0.354	0.010
C9	75-85	0.609	0.583	0.546	0.579	0.032
C9	105-115	0.490	0.478	0.493	0.487	0.008
C9	145-155	0.594	0.574	0.580	0.583	0.010
C9	295-300	0.387	0.401	0.395	0.394	0.007
C9	300-310	0.420	0.415	0.449	0.428	0.018
C9	405-420	0.435	0.437	0.445	0.439	0.005
C6	5-10	0.441	0.446	0.437	0.441	0.005
C6	25-30	0.544	0.585	0.564	0.564	0.021
C6	35-40	0.478	0.478	0.476	0.477	0.001
C6	45-50	0.445	0.438	0.436	0.440	0.005
C6	55-60	0.480	0.496	0.493	0.490	0.009
C6	75-80	0.511	0.496	0.506	0.504	0.008
C6	180-190	0.426	0.487	-	0.457	0.043
C6	210-200	0.344	0.346	0.352	0.347	0.004
C6	95-105	0.437	0.414	0.387	0.413	0.025
C6	350-360	0.346	0.333	-	0.340	0.009
C6	450-460	0.368	0.350	-	0.359	0.013
C1	0-10	0.736	0.725	0.754	0.738	0.015
C1	20-30	0.369	0.367	0.367	0.368	0.001
C1	30-40	0.412	0.416	0.410	0.413	0.003
C1	40-50	0.376	0.382	0.381	0.380	0.003
Gulf of Mexico						
BH	Surface	3.099	2.990	3.150	3.080	0.082
BH	Surface	5.140	5.200	-	5.170	0.042
BH	Surface	9.160	9.640	-	9.400	0.339
BH	Surface	3.850	3.550	3.560	3.653	0.170

BH	Surface	1.230	1.280	1.230	1.247	0.029
BH	Surface	3.920	4.260	3.860	4.013	0.216
GC234	Surface	4.290	4.930	-	4.610	0.453
GC234	Surface	14.780	11.960	12.660	13.133	1.468
GC234	Surface	1.290	1.290	1.220	1.267	0.040
GC234	Surface	12.800	20.870	17.570	17.080	4.057
GC234	Surface	1.550	1.570	1.450	1.523	0.064
GC234	Surface	4.690	4.930	4.930	4.850	0.139

Sediment grain analysis was conducted on Cascadia Margin cores from sites C1, C7 and C9. With the exception of the surface depth of C1 all samples were well sorted silt and clay. The C1 surface sample contained 59.4% sand. Particle size phi 9 (1.95  $\mu$ m) ranged from 20.77 to 45.41% for all of the samples that were analyzed. Vibration in the laboratory prohibited grain size analysis smaller the phi 9.

Table 3: Grain size analysis of cores from Cascadia Margin sites C1, C7 and C9. Data presented represent the percent of the sediment particles that fall in the range of phi size classes.

Sample	Depth (cm)	phi							
		4	4.5	5	5.5	6	7	8	9
C9	5-10	100	94.72	88.38	81.71	75.01	61.32	48.17	36.83
C9	15-20	100	97.27	93.24	86.63	81.20	66.05	51.87	35.84
C9	35-40	100	95.61	92.52	93.99	86.05	74.43	59.83	45.01
C9	45-50	100	97.49	92.47	84.52	76.84	67.28	41.26	30.05
C9	75-85	100	99.84	98.42	92.78	88.18	69.97	52.64	35.76
C9	105-120	100	99.57	97.46	90.00	81.45	63.82	47.01	32.75
C9	145-155	100	96.80	93.78	88.63	81.95	67.12	51.27	39.49
C9	295-300	100	90.19	87.46	60.91	73.84	59.41	51.99	34.81
C9	300-310	100	91.32	88.97	80.82	74.21	61.11	51.46	37.20
C1	0-10	100	94.66	92.06	92.25	87.12	78.59	63.18	45.41
C1	20-30	100	96.64	92.46	84.78	58.10	49.80	40.03	24.71
C1	30-40	100	94.84	90.37	84.18	78.44	61.12	44.65	29.41
C1	40-50	100	98.63	94.15	85.70	78.86	64.47	46.60	30.72
C7	200	100	98.01	94.98	90.83	83.79	65.79	49.06	31.09
C7	270	100	95.66	90.58	82.81	76.79	60.68	45.19	30.77
C7	280	100	98.67	93.84	86.29	76.91	58.50	41.35	26.03
C7	300	100	93.90	86.53	76.88	68.37	51.55	35.87	20.77

## b). Hydrate Gas Content

Hydrate content was analyzed on samples from GOM and compared to HMMV (Table 4). Samples from the HMMV contained 99.5% methane. The GOM hydrates ranged from 29.7 to 73.5% methane, 8.6 to 15.3% ethane, 11.6 to 36.6% propane, and 2.0 to 9.7% isobutane. Butane, pentane and hexane ranged from 0.1 to 3.2%. In the Gulf of Mexico yellow surface hydrates contained oil between the lattice. Comparison of hydrates with and without oil saturated lattice showed that there was not a difference in the gas content. However, there is a difference in the gas content between the two sample regions of Bush Hill and Green Canyon with samples at Bush Hill containing a higher percentage of methane and Green Canyon more ethane and isobutane. Further investigation is needed to determine the factors that control variation in the lattice content and saturation. Hexane was observed in one hydrate with a relatively low methane content and a high propane concentration. This suggests that this is hydrate structure H and is currently being confirmed with x-ray diffraction at the DOE Argonne National Laboratory. The HMMV hydrates have been confirmed to contain structure I, while the GOM is a mix structure I and II and possibly structure H.

Table 4: Hydrate content of samples taken from the Haakon Mosby Mud Volcano and the Texas-Louisiana Shelf. Stations named Bush Hill and Green Canyon are located in the GOM. Gases from methane (C1) to hexane (C6) were compared for the present composition.

Sample ID	% Hydrocarbon composition						
	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	<i>i</i> -C <sub>4</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>
Haakon Mosby MV	99.5	0.1	0.1	0.1	0.1	0.0	0.1
Bush Hill White	72.1	11.5	13.1	2.4	1.0	0.0	0.0
Bush Hill Yellow	73.5	11.5	11.6	2.0	1.0	0.1	0.2
Green Canyon White	66.5	8.9	15.8	7.2	1.4	0.1	0.1
Green Canyon Yellow	69.5	8.6	15.2	5.4	1.2	0.0	0.0
Bush Hill	29.7	15.3	36.6	9.7	4.0	3.2	1.6

## c). $\delta^{13}\text{C}$ Hydrates

Stable carbon isotope analysis is employed to determine the relative contribution of biogenic and thermogenic source(s) to the gases in hydrates. Thermogenic methane is more isotopically enriched in  $\text{C}^{13}$  with an approximate range in values from  $-30$  to  $-45$  ‰. Biogenic methane is substantially depleted in  $\text{C}^{13}$  with values that typically range between  $-60$  to  $-70$  ‰ and have been measured to be more depleted in sites where the methane is recycled in the sediments. For this document  $\delta^{13}\text{C}$  is compared from the HMMV, CM, and GOM. The hydrates from the GOM show a strong thermogenic isotope signature in the ethane to pentane gases (Figure 1). Pentane was isotopically enriched relative to the other gases with an average of  $-24.75 \pm 1.67$  for 8 hydrate samples. The gases with lower molecular weights had depleted isotope values with ethane  $\delta^{13}\text{C}$  the lowest averaging  $-29.14 \pm 0.62$  ‰ for 18 hydrate samples. An interesting result of the analysis was the

difference in the ranges of the GOM gases, where ethane to pentane variation was low, the methane variation was greater. Methane isotope ratios varied from  $-49.37$  to  $-33.49\text{‰}$  with an average and standard deviation of  $-45.45 \pm 3.96\text{‰}$ . This result suggests a variation in the biogenic cycling of the methane between the 18 samples. This statement is supported with the large  $\delta^{13}\text{C}$  variation in the  $\text{CO}_2$  found in the hydrates. In 17 hydrate samples the values ranged from  $-16.77$  to  $18.83\text{‰}$ . The  $\text{CO}_2$  is expected to become more enriched in  $\text{C}^{13}$  as it is reduced to methane by bacteria.

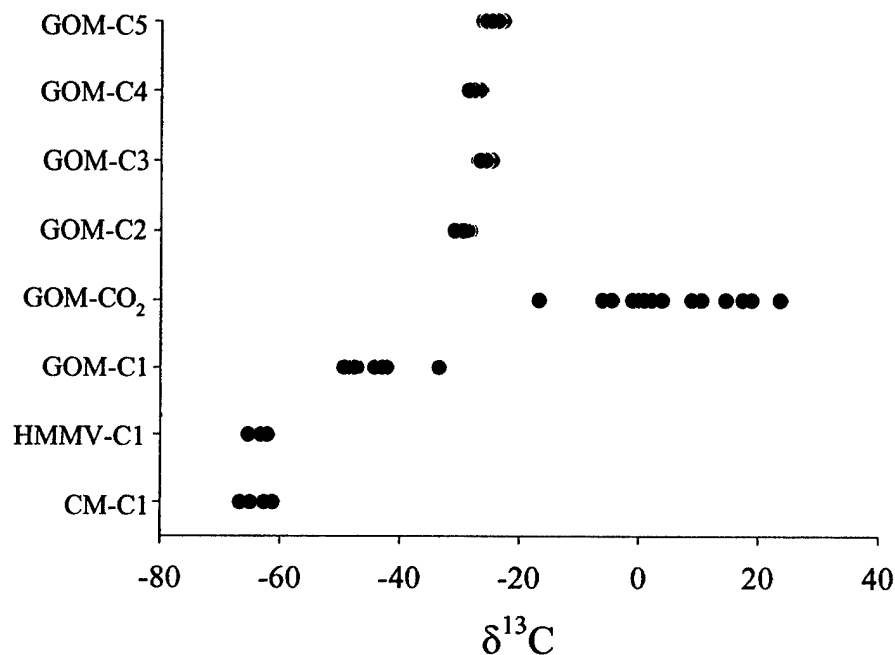


Figure 1: Stable carbon isotope analysis of hydrate gases. Samples are from the Gulf of Mexico (GOM), Haakon-Mosby Mud Volcano (HMMV) and the Cascadia Margin (CM). Gases analyzed include methane to pentane (C1 to C5) and  $\text{CO}_2$ .

The HMMV and CM hydrates contained only methane (Table 4). The methane  $\delta^{13}\text{C}$  ranged from  $-65.36$  to  $-62.14\text{‰}$  in 6 hydrates from the HMMV and  $-66.64$  to  $-61.27\text{‰}$  for six samples from the Cascadia Margin (Figure 1). These results coupled with the analysis of the hydrate content indicate that methane in hydrates at these sites is formed biogenically.

#### d). $\delta^{13}\text{C}$ Organic Sediments

Analysis of the sediment carbon sources was conducted to advance understanding of the methane hydrate content and lattice saturation. The  $\delta^{13}\text{C}$  analysis of the sediments provides information on the primary sources of carbon in the sediment. Stable carbon isotope values in the range of  $-18$  to  $-22\text{‰}$  in these study sites represent carbon from ocean water column primary production. The methane cycling into the sediment organic carbon has a complex series of cycles that can influence these isotope signatures. More

$C^{13}$  depleted values, ranging from  $-30$  to  $-40\text{‰}$  indicates thermogenic methane. Biogenic methane has potential to result in isotope signatures, more depleted, in the range of the methane measured in CM and HMMV hydrates. Another cycle that can contribute to the  $C^{13}$  depleted signatures is the oxidation of methane and fixation of  $CO_2$  (chemosynthesis). Additional tracers are needed to determine the sources of carbon in these sediments. The current stable carbon isotope data suggests that there is a large variation in the carbon cycles in the hydrate regions. Figure 2 presents  $\delta^{13}C$  for organic sediments from HMMV, CM and GOM. The control value is from the GOM, outside regions with hydrates. This value at  $-21.50\text{‰}$  represents a strong water column phytoplankton production input (Figure 2). At many of the sites that were surveyed the  $\delta^{13}C$  are substantially lower than the control site. The most depleted  $\delta^{13}C$  signatures are observed in the HMMV and GOM-BP. The isotope ratios at the individual sites are variable suggesting that there is a large range in the methane cycling and the contribution to organic matter in the sediments. Future work will apply additional tracers to understand this variation and the influence on hydrate formation, stability and lattice saturation.

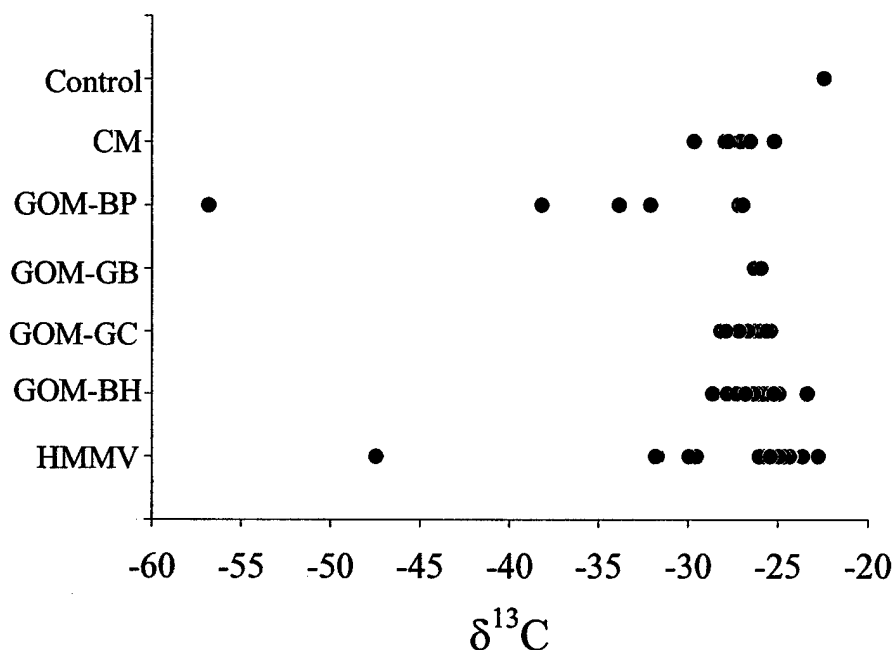


Figure 2: Stable carbon isotope analysis of organic carbon in shallow sediments through regions surrounding active methane hydrate beds. Samples were taken in the Gulf of Mexico (GOM), Cascadia Margin (CM), and Haakon-Mosby Mud Volcano (HMMV). Different sites sampled in the Gulf of Mexico include a brine pool (BP), Garden Bank (GB), Bush Hill (BH), and Green Canyon (GC).

Vertical  $\delta^{13}C$  profiles of organic carbon in the sediments were analyzed in hydrate beds on the Cascadia Margin (Figure 3). Cores 1, 6, and 7 were taken in an active hydrate region while core 9 was taken outside of the active hydrate bed. The segments of core 7 that are presented were in regions where hydrates were found. There was a wide range in  $\delta^{13}C$  values between the sites and through the cores, with  $\delta^{13}C$  values between  $-29.68$  and  $-$

18.67. The sub-samples from core 7 were observed to have the most depleted  $C^{13}$ . Core 6 was found to have the most enriched  $C^{13}$  values, indicating ocean phytoplankton was a significant carbon source. As noted between different sites and ocean regions, the large range in values through the vertical profiles indicates that there was a large variation in methane contribution to the sediment carbon cycle. Future work will employ carbon isotope analysis of DIC and bacterial biomarkers (hopanes) to assess the variation in the sediment organic carbon isotope analysis.

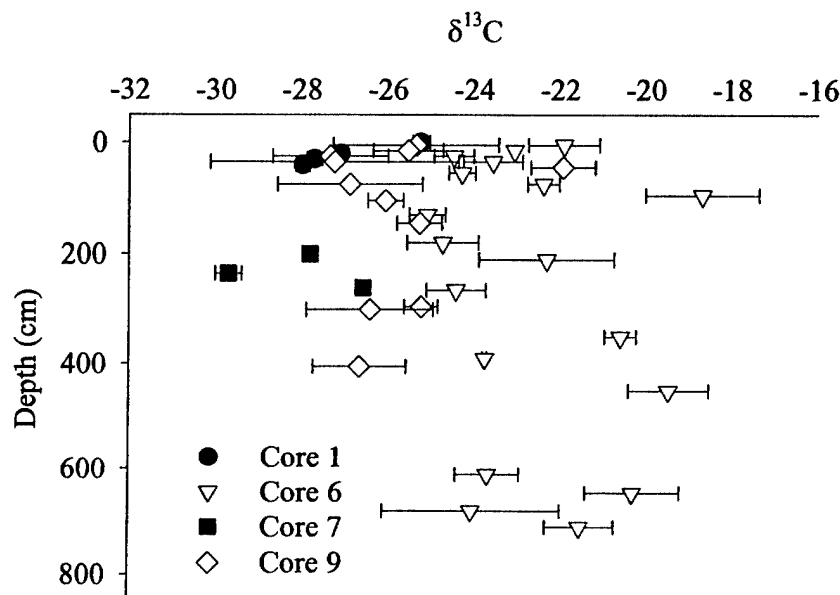


Figure 3: Stable carbon isotope analysis of sediment organic carbon on samples from the Cascadia Margin.

#### e). $\delta^{13}C$ Carbonates

Stable carbon isotope analysis of carbonates was not completed because of technical problems with the IRMS. A complete data set will be provided when the system is repaired. The existing data shows an interesting trend in the  $\delta^{13}C$  through the vertical profile, with values ranging between 2.82 and  $-14.77\text{‰}$  (Table 5). The  $C^{13}$  enriched values, 2.82 to  $-2.47\text{‰}$  indicate the carbonate is a biogenic source. At 130-140 cm into the core the  $C^{13}$  depleted value of  $-14.77\text{‰}$  suggests the formation of carbonate is partially from authigenic cycles. Authigenic carbonate has been measured to be  $C^{13}$  depleted at approximately  $-60\text{‰}$  on the Blake Ridge. Completion of this data will assist in analysis of the amount of methane this is oxidized through the water column.

Table 5: Preliminary analysis of sediment bicarbonate  $\delta^{13}\text{C}$  in Core 6 from the Cascadia Margin.

Sample	Depth (cm)	$\delta^{13}\text{C}$	$\delta^{13}\text{C}$	$\delta^{13}\text{C}$	Average	s.d.
Core 6	25-30	3.49	3.15	1.82	2.82	0.88
Core 6	130-140	-13.97	-14.62	-15.71	-14.77	0.88
Core 6	390-400	-6.14	-5.52	n.d.	-5.83	0.44
Core 6	450-460	-0.39	-1.9	n.d.	-1.15	1.07
Core 6	645-655	-4.81	-4.89	-4.79	-4.83	0.05
Core 6	680-690	-2.47	n.d.	n.d.	-2.47	-

## 6. Summary

- a). The percent organic carbon in CM sediments was low. Values ranged from 0.340 to 0.738%. In comparison the GOM samples ranged from 1.25 to 17.08%. The high carbon content in this system results from petroleum seepage.
- b). The sediments consisted of well sorted silt and clay. Particle size analysis of cores from the CM found that between 20.77 to 45.41% of the grains were 1.95  $\mu\text{m}$  or smaller.
- c). The methane content in hydrates from the Gulf of Mexico varied between 73.5 and 29.7%. There was a large concentration of propane in the GOM hydrates indicating thermogenic origin of the gases.
- d). Stable carbon isotope analysis of hydrate methane on HMMV and CM samples shows that the source is biogenic. The isotope analysis of the gases from the GOM samples indicates a thermogenic origin and biogenic cycling of the methane.
- e). Stable carbon isotope analysis of the organic matter in sediments from GOM, CM and HMMV show a high variation in values. Carbon sources for this organic matter include marine phytoplankton, biogenic methane and thermogenic methane. In many of the samples methane is a large fraction of the sediment carbon cycling.
- f). Preliminary stable carbon isotope analysis of the carbonate in sediments suggests that the source is dominantly biogenic. In one sample a more  $\text{C}^{13}$  depleted signature indicates authigenic input.

## 7. Literature Cited

- Borowski, W.S., C.K. Paull, W. Ussler III. 1996. Marine pore-water sulfate profiles indicate in situ methane flux from underlying gas hydrate. *Geology* **24**, 655-658.
- Borowski, W.S., C.K. Paull, W. Ussler III. 1997. Carbon cycling within the upper methanogenic zone of continental rise sediments: An example from the methane-rich sediments overlying the Blake Ridge gas hydrate deposits. *Mar. Chem.* **57**, 299-311.

Estep, M.L., F.R. Tabita, P.L. Parker, and C. Van Baalen. 1978. Carbon isotope fractionation by ribulose 1,5-bisphosphate carboxylase from various organisms. *Plant Physiol* **61**, 680-687.

Fogel, M.L. and L.A. Cifuentes. 1993. Isotopic fractionation during photosynthesis: Interpretation for the fossil record. In *Organic Geochemistry*, Eds. M. Engel and S. A. Macko - Eds.

Galehouse, J. S. 1971. Sedimentation analysis. In *Procedures in Sedimentary Petrology* (ed. R. Carver) John Wiley pp. 69-94.

Gearing, P., F.E. Plucker, and P.L. Parker. 1977. Organic carbon stable isotope ratios of continental margin sediments. *Mar. Chem.* **5**, 251-266.

Ingram, R. 1971. Sieve Analysis. In *Procedures in Sedimentary Petrology* (ed. R. Carver) John Wiley pp. 49-67.

Parsons, T.R., Y. Maita, and C.M. Lalli. 1984. A manual of chemical and biological methods of seawater analysis. Pergamon Press, New York.

Rau, G.H., T. Takahashi, and D.J. Des Marais. 1989. Latitudinal variation in plankton  $\delta^{13}\text{C}$ : implication for  $\text{CO}_2$  and productivity in past oceans. *Nature* **341**, 516-518.

Sackett, W.M. 1991. A history of the  $\delta^{13}\text{C}$  composition of oceanic plankton. *Mar. Chem.* **34**, 153-156.

Whelan, T., M.W. Sackett, and C.R. Benedict. 1973. Enzymatic fractionation of carbon isotopes by phosphoenolpyruvate carboxylase from  $\text{C}_4$  plants. *Plant Physiol.* **51**, 1051-1054.